

Mass transport study of Nafion[®] coatings saturated with [Os(bpy)₃]²⁺ by an electrochemical quartz crystal microbalance

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Abstract

Ion transport out of and into the Nafion[®] coating on an electrode during the electrochemical processes was studied using an electrochemical quartz crystal microbalance (EQCM). After saturated loading of [Os(bpy)₃]²⁺, the first cyclic voltammogram (CV) initiated from the lower limit showed an anodic peak around 0.85 V vs. Ag|AgCl which, according to a previous study by Anson's group, corresponds to ejection of the [Os(bpy)₃]³⁺ complex from the Nafion[®] coating. However, the frequency change–potential ($\Delta f-E$) curve obtained by EQCM showed an increase in the mass on the first positive scan. These contradictory results can be explained by the movement of water molecules in a direction opposite to that of [Os(bpy)₃]³⁺ complexes. After a number of successive cycles, a steady state voltammogram was obtained. In this case the mass change was attributed mainly to the movement of the hydrated electroinactive counter-cations of the supporting electrolyte. The hydration numbers for two of the supporting electrolyte cations are in good agreement with the published results.

Keywords: Membrane electrodes; Charge transport mediators; Mass transport; Electrochemical quartz crystal microbalance

1. Introduction

Perfluorinated polyelectrolyte membranes, including Nafion[®], have been widely used both in industry and in chemistry research [1–3]. In particular, the groups led by Anson [4–6], Bard [7–9] and Martin [10,11] have employed Nafion[®] extensively in various studies of the charge transport mechanisms with various redox couples which have been incorporated into Nafion[®] as charge transport mediators. These mediators include [Ru(bpy)₃]²⁺, [Os(bpy)₃]²⁺, [Ru(NH₃)₆]²⁺, and methyl viologen.

One of the problems with Nafion[®] studies is that materials retained in the hydrophobic domains exhibit sluggish transport rates. This can have deleterious effects in an electrocatalytic cycle if the active site resides mainly in the hydrophobic domain. The solvent swelling properties of Nafion[®] membranes depend on the nature of the counter-ion present, its solvation properties and the pre-treatment [12].

Using various electrochemical methods and scanning

electrochemical microscopy (SECM), Anson and coworkers [13–15] recently showed that [Os(bpy)₃]³⁺ complexes are ejected from Nafion[®] coatings saturated with [Os(bpy)₃]²⁺ during electrochemical oxidation. However, they did not give a detailed discussion of the mass transport behavior during electrochemical processes.

We report here the mass transport behavior in Nafion coatings determined concurrently with electrochemical measurements. It was found that the mass of [Os(bpy)₃]²⁺-saturated Nafion[®] membrane electrodes varies with the number of cycles after the initiation of potential scan and approaches a steady state.

2. Experimental

A solution of 0.5% Nafion[®] (Aldrich) (mass per monovalent charge, 1100 g) in ethanol was diluted 10 times with alcohol, and Nafion[®] coatings were prepared by slow evaporation of this solution dropped on the electrode in a box saturated with alcohol vapor. The density of sulfonate sites was calculated as 1.2×10^{-8} mol cm⁻² and the thickness of the films was estimated as about 0.2 μ m.

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$[\text{Os}(\text{bpy})_3]\text{Cl}_2$ (bpy = 2,2'-bipyridine) was prepared from K_2OsCl_6 and bipyridyl in glycerol by a standard method [16]. Deionized water was used throughout the experiment. The complexes were incorporated by contacting the coating with an osmium complex solution in appropriate supporting electrolytes such as H_2SO_4 , LiNO_3 and Na_2SO_4 .

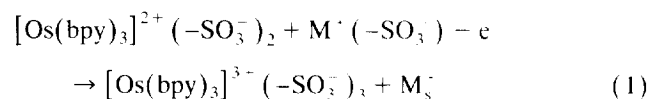
A commercial potentiostat (BAS) with a glassy carbon electrode (diameter 3 mm) was used for survey CV. The EQCM instrumentation [17], including an RF oscillator [18], a frequency counter and a potentiostat [17], was built in the laboratory and controlled by a PC/AT computer through a home-made interface board. The control software was written in Assembler and C language. The working electrodes in the EQCM experiments were connected to real ground, and the current was measured from the counter-electrode [17]. The potentials were measured versus a $\text{Ag}|\text{AgCl}|\text{KCl}(\text{sat})$ reference electrode. AT-cut quartz crystals (10.0 MHz) were purchased from International Crystal Manufacturer Inc., Oklahoma, OK. Gold electrodes were deposited in a keyhole pattern on both sides of the crystals and the total area exposed to the solution was ca. 0.2 cm^2 . The crystal was attached with thin gold strips to an electrochemical cell designed specifically for our purpose. The sensitivity of this system was calculated to be 0.9 ng Hz^{-1} .

The viscoelastic properties of the Nafion[®] films during the electrochemical processes were measured with a high frequency response analyzer (Schlumberger SI 1255). Experiments were conducted in ambient laboratory conditions.

3. Results and discussion

$[\text{Os}(\text{bpy})_3]^{2+}$ complex is frequently used as a mediator for charge transfer studies in polyelectrolytes such as Nafion[®]. Anson and coworkers [13–15] have studied the Nafion[®] + $[\text{Os}(\text{bpy})_3]^{2+}$ system extensively using various electrochemical methods and SECM. Positively charged metal complexes are incorporated by electrostatic attraction between complex cations and negatively charged sulfonate sites in Nafion[®], and the redox conductivity of Nafion[®] coatings increases as redox couples are incorporated.

The number of positively charged complexes incorporated is limited by the number of sulfonate sites and the charge on the complexes. When two-thirds of the total quantity of fixed sulfonate sites within the coating are occupied by $[\text{Os}(\text{bpy})_3]^{2+}$, the following electrochemical oxidation reaction occurs:



where M^+ is a monovalent cation, $(-\text{SO}_3^-)$ denotes sulfonate sites in Nafion[®] and the subscript s denotes the

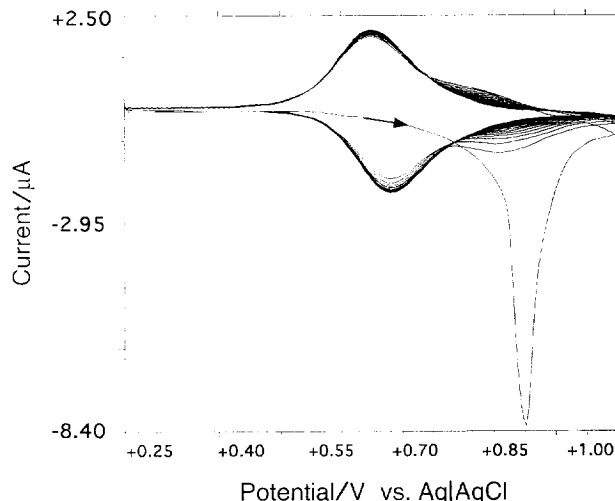
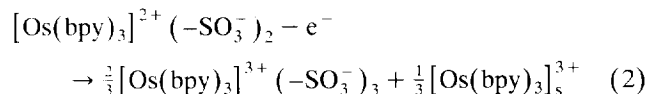


Fig. 1. Survey CV of a Nafion[®] coating saturated with $[\text{Os}(\text{bpy})_3]^{2+}$. A glassy carbon working electrode (diameter 3 mm) was used, the supporting electrolyte was 0.1 M CH_3COONa and the scan rate was 10 mV s^{-1} .

solution phase. M^+ is assumed to move freely between the permselective coating and the solution to maintain electroneutrality during the electrochemical oxidation process because it is much more mobile than the osmium complexes. When Nafion[®] is saturated with $[\text{Os}(\text{bpy})_3]^{2+}$, the oxidation reaction is represented by



where $[\text{Os}(\text{bpy})_3]_s^{3+}$ denotes the Os(III) complexes ejected from the Nafion[®] coating to maintain the charge balance.

When a fresh Nafion[®] coating saturated with $[\text{Os}(\text{bpy})_3]^{2+}$ is subject to a potential scan starting from the lower limit in the positive direction, the CV as shown in Fig. 1 is observed. According to Lee and Anson [15], an anodic peak which corresponds to the ejection of excess osmium complexes according to Eq. (2) appears near 0.85 V during the first positive scan. It seemed to be irreversible because the corresponding cathodic peak is much smaller and a pair of symmetrical peaks appeared near 0.6 V. When potential cycling was repeated, the peak near 0.85 V rapidly decreased and a pair of reversible peaks corresponding to Eq. (1) developed at 0.62 V.

In short, if Nafion[®] coatings are saturated with $[\text{Os}(\text{bpy})_3]^{2+}$ complexes, one-third of them should be ejected, mainly in the form of $[\text{Os}(\text{bpy})_3]^{3+}$, during the positive scan. Thus a very simple response is expected for the Nafion[®] + $[\text{Os}(\text{bpy})_3]^{2+}$ system in EQCM study, reflecting a decrease in the mass of the electrode. In particular, during the first positive scan of $[\text{Os}(\text{bpy})_3]^{2+}$ -saturated Nafion[®] film, the greatest mass decrease is expected to match the CV result.

Fig. 2 shows the EQCM frequency response for a Nafion[®] coating saturated with $[\text{Os}(\text{bpy})_3]^{2+}$ during the first 1600 s of potential cycling between 0.2 and 1.0 V,

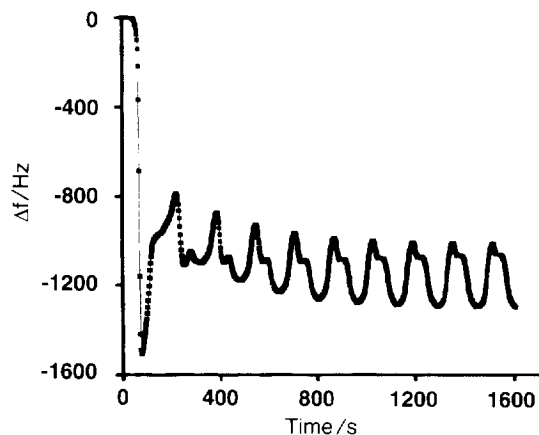


Fig. 2. Frequency response for a Nafion[®] coating saturated with $[\text{Os}(\text{bpy})_3]^{2+}$ during the first 1600 s of potential cycling between 0.2 and 1.0 V, initiated at 0.2 V; supporting electrolyte, 0.05 M H_2SO_4 ; scan rate, 10 mV s^{-1} .

initiated at 0.2 V. The variation in frequency parallels the potential cycling.

The frequency change–potential (Δf – E) curve and the CV for the first cycle in Fig. 2 are shown in Fig. 3. The Δf – E curve shows contradictory results from those predicted by in Eq. (2), i.e. the mass on electrode increases

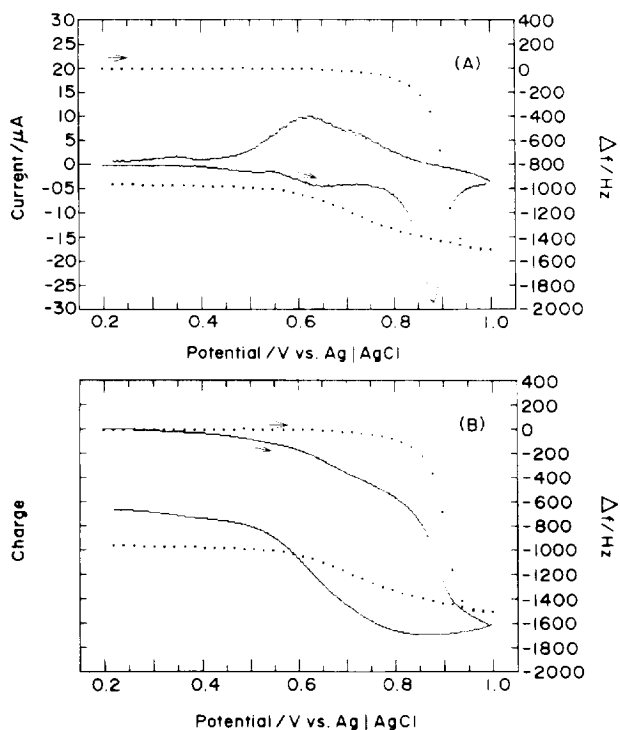


Fig. 3. (A) Cyclic voltammogram and the corresponding frequency response and (B) charge and frequency response of a Nafion[®] coating saturated with $[\text{Os}(\text{bpy})_3]^{2+}$ in 0.05 M H_2SO_4 recorded during the first potential cycle. The frequency response is shown by the large dots. The charge was obtained by numerical integration of current and is recorded on an arbitrary scale for comparison with the frequency response. Other conditions are as in Fig. 2.

substantially during the first positive scan and returns almost to its original value during the subsequent negative scan. In order for the CV and EQCM results to be consistent, something much heavier than the total mass ejected must be introduced when the osmium complexes are removed from the Nafion[®] coating on the electrode. In this study the following should be remembered with respect to transport of charged species of Nafion[®] coatings. Counter-anions cannot be inserted into the Nafion[®] coating in any way because these coatings are almost ideally permselective [13,19]. We confirmed that this was true, at least for the Nafion[®] coatings used in this study, by examining the effect of the chloride ion on the corrosion of a gold surface as was done by Striebel et al. [20]. Almost no corrosion by the chloride ion was observed for a gold electrode covered with $[\text{Os}(\text{bpy})_3]^{2+}$ -loaded Nafion[®] coatings, which shows that anions cannot enter an $[\text{Os}(\text{bpy})_3]^{2+}$ -loaded Nafion[®] coating on a gold electrode and that Nafion[®] coatings themselves have excellent permselectivity. Therefore it is obvious that the counter-cations must be ejected to maintain charge neutrality during electrochemical oxidation.

It is well known [12,21] that Nafion[®] exists in segregated phases with hydrophobic (fluorocarbon) and hydrophilic (clusters of sulfonate sites) domains connected by an interfacial region as in other polyelectrolytes. The cluster size depends strongly on the water content inside the polymer. This is related not only to the hydration state of the charged species inside the Nafion[®] coating, but also to the electrolyte concentration which affects the value of the water activity in the membrane + solution system [21].

Thus a possible explanation for the inconsistency between mass change and current during the first positive scan is that there is movement of water molecules. Electro-osmosis is not considered as a contributing factor to the movement of water because it has the opposite effect. Instead, the increase in the charge on the osmium complexes after oxidation may have a major effect on solvent movement. When three sulfonate groups in the cluster are bound to $[\text{Os}(\text{bpy})_3]^{3+}$ after oxidation, the degree of freedom of the water molecules in the cluster is expected to be lost to some extent. Enforced ion–water interactions in the Nafion[®] coating tend to reduce water activity effectively and to promote greater osmotic uptake of water and a larger osmotic pressure according to [22].

$$\pi V_{\text{H}_2\text{O}} = -RT \ln(a_{\text{H}_2\text{O}}) \quad (3)$$

where π is the osmotic pressure, $V_{\text{H}_2\text{O}}$ is the molar partial volume of water and $a_{\text{H}_2\text{O}}$ is the activity of water inside the coating.

The mass change in the first positive scan corresponds to ca. 20 water molecules per sulfonate site to account for the ejection of $[\text{Os}(\text{bpy})_3]^{2+}$. It is not surprising that 20 water molecules per sulfonate site moved into the coating since it has been reported [23] that 24 molecules of water with a chloride ion are moved into or out of

[Os(bpy)₂(PVP)₁₀Cl]Cl coatings during oxidation or reduction. In Fig. 3(B), the mass change seems to be delayed slightly with respect to the charge change, which is believed to be due to the fact that the diffusion coefficient of Os(III) in the Nafion coating is not large enough to follow the charge transfer rate even if the diffusion coefficient of the osmium complexes in the Nafion[®] films increases with increasing coverage of the redox couple in the coatings [14,15].

When the potential sweep was reversed, some of the ejected complexes were returned into the coating after reduction, resulting in the egress of water molecules. If an excess of water molecules is repelled, the mass on the electrode may decrease despite the introduction of complexes into the coating, as shown in Fig. 3(A). Sometimes mass continues to increase at the beginning of the negative scan, but it soon begins to decrease as shown in Fig. 3(A). The decrease in mass during the negative scan is less than the increase in mass during the first positive scan, and this is attributed to the fact that most of the ejected Os(III) diffuses out beyond the diffusion layer so that only a fraction of the ejected complexes can return to the coating during the following negative scan. The rapid diminution of the peak in CV near 0.85 V during the first few cycles can be explained in a similar manner. When the potential was returned to the lower limit at which the initial potential scan was started, the mass of the coating was found to be increased (comparing the frequencies before and after potential scan) even though a substantial amount of osmium complexes have been ejected. This increase in mass after a complete cycle corresponds to ca. 14 water molecules per sulfonate site. Thus we can conclude that ca. 20 water molecules per sulfonate site were introduced during the first positive scan and ca. six water molecules per site were ejected during the following negative scan.

Fig. 4(A) shows a cyclic voltammogram and the corresponding frequency response for the following 3.5 cycles in which the anodic peak around 0.88 V decreased substantially and a pair of reversible peaks developed around 0.62 V. The Δf - E curves show that the mass increase during the positive scan as substantially reduced compared with that of the first scan. The difference in mass change gradually reduced during repeated cycling between the limiting potentials and eventually the mass decreased. The behavior during the negative scan was just the opposite. The mass measured at the upper limit began to exceed that measured at the lower limit, and this trend became clearer with repeated potential cycling. It is believed that the reorganization of the Nafion[®] coating and the diffusion layer approaches a steady state.

The frequency response curve became steady after several cycles, and in this situation Eq. (1) is exactly satisfied (Figs. 2 and 5(A)). At the upper limit all sulfonate sites were occupied by osmium complexes, and at the lower limit two-thirds of the total number of sulfonate sites were bound to complexes and one-third were occupied by

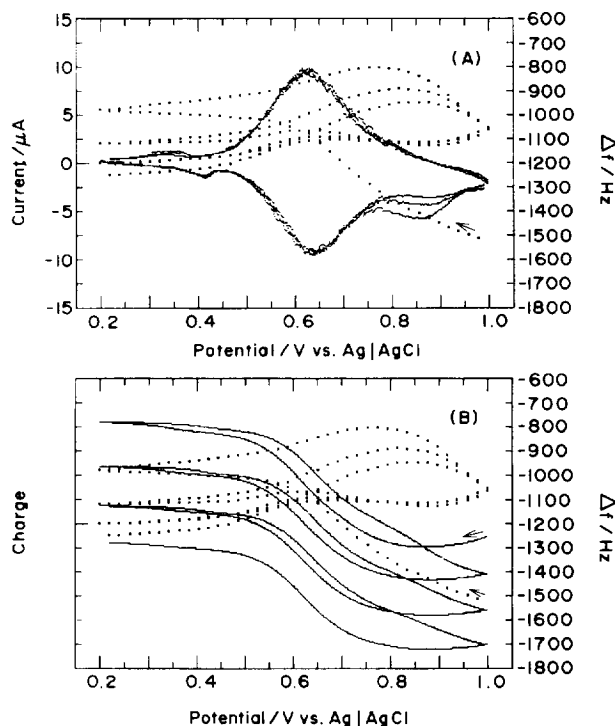


Fig. 4. (A) Cyclic voltammogram and the corresponding frequency response and (B) charge and frequency response of the Nafion[®] coating for the negative half-cycle in Fig. 3(A) and the next three cycles after recording Fig. 3. The charge was obtained by numerical integration of the current and recorded on an arbitrary scale for comparison with the frequency response. Other conditions are the same as in Fig. 2.

monovalent counter-cations supplied by the supporting electrolyte. In this case, the mass difference between the upper and lower limits is constant, and after repeated potential cycles the difference between the mass changes measured at the potential limits became zero because only the monovalent counter-cation is transported into and out of the coating. In other words, mass change is dominated by the monovalent counter-cation which is expected to move in the hydrated form. This mass change is well matched with the estimate from the unit mass of cations in the hydrated form and the total quantity of counter-ions moving, as estimated from the CVs. When H₂SO₄, LiNO₃ and Na₂SO₄ solutions were used as the supporting electrolyte, the hydration numbers for H⁺, Li⁺ and Na⁺ were estimated to be 5.5, 12.5 and 6.4, respectively, compared with their literature values of 5.5, 12, and 7 [24]. This means that this mass change is due mainly to the transport of hydrated monovalent counter-cations and not to the movement of osmium complexes.

Examination of Fig. 5(B), in which the movement of monovalent counter-ions provides the main contribution to mass transport, shows that the oxidation and ejection of counter-cations occurred simultaneously and that the incorporation of counter-ions lagged behind reduction. The delay in reduction is believed to reflect the time required to reverse the direction of diffusion and was compensated

at the slower scan rate of 5 mV s^{-1} (Fig. 5(C)). However, in Fig. 4(B) it is impossible to compare the two phenomena because this figure shows the mixed behavior of solvent and complex movement, and movement of monovalent counter-ions in the opposite direction.

Fig. 6 shows frequency data measured at 0.2 V for each potential cycle. It can be seen that the mass on the electrode increases rapidly, approaching a limiting value with the number of cycles. The mass difference between the initial and final states corresponds to about 18 molecules of water per sulfonate. A possible explanation for this behavior is insufficient hydration. However, the explanation that this mass difference is due to insufficient hydra-

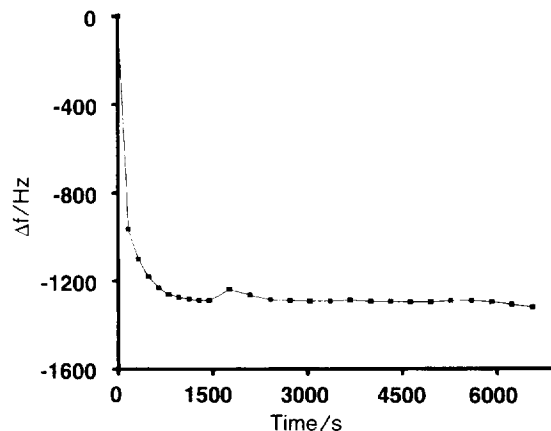


Fig. 6. The variation of frequency response at 0.2 V after each potential cycle, taken from the data set used in Fig. 2.

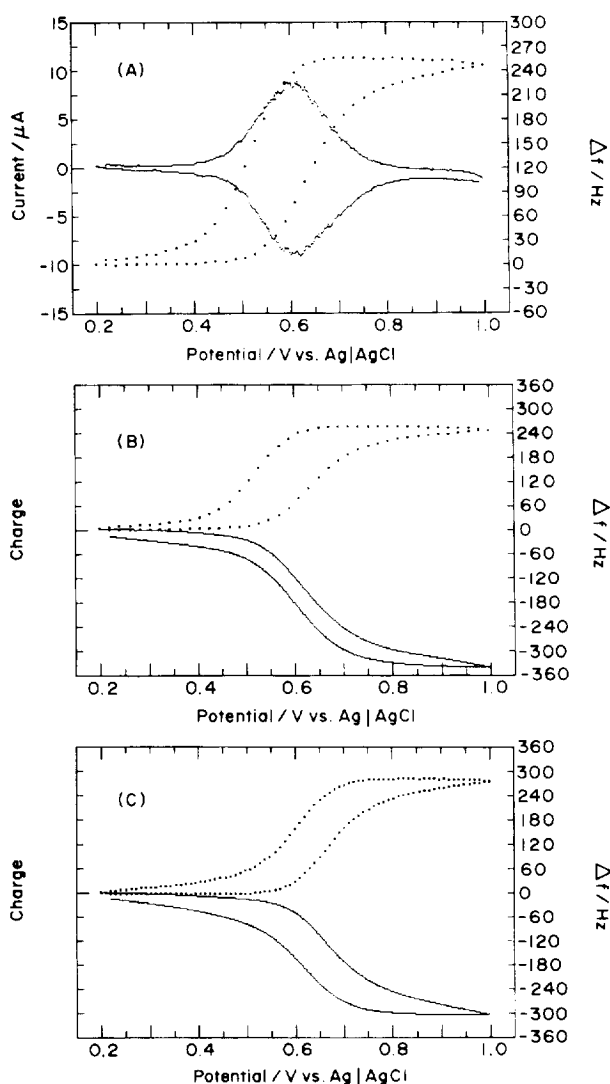


Fig. 5. (A) Cyclic voltammogram and the corresponding frequency response and (B) charge and the frequency response of the Nafion[®] coating recorded in a steady-state condition. Other conditions are the same as in Fig. 2. (C) Charge and frequency response recorded at a slower scan rate of 5 mV s^{-1} . The charge was obtained by numerical integration of the current and recorded on an arbitrary scale for comparison with the frequency response. Other conditions are the same as in Fig. 5 (B).

tion of the sulfonate site at the initial stage of experiment is not plausible because almost the same frequency response as that in Fig. 3(A) could be reproduced after three repetitive saturation–ejection cycles, which means that the coating was sufficiently swollen at the initial stage. If the maximum hydration number per sulfonate site is assumed to be 28, as in the case of the 117 Nafion[®] membrane [21], the sulfonate sites of the Nafion[®] coating used in this experiment were initially hydrated by only 10 water molecules. According to Escoubes and Pineri [25], a Nafion[®] coating swollen by 10 water molecules per sulfonate site is obtainable in 1 atm water vapor. This amount of water (108 molecules of water per osmium complex) is too large to be considered as representing just the molar volume of the Os(II) complex, which has a larger molar volume than that of a water molecule, even if the empty space resulting from ejection of osmium complexes is included. The contribution of the Os(II) complex to the total volume of water introduced is about 13% if it is assumed to be spherical with a radius of about 9.5 \AA [26]. Thus it is difficult to accept that the ingress of water is closely related to compensation of the void space due to movement of the Os(II) complex out of the coating.

It has recently been reported that the viscoelastic property of the polymer films affects the frequency of the EQCM [27]. In order to check the effect of the viscoelasticity of the Nafion[®] coating on the frequency change, the impedance change versus frequency near resonance was measured for three conditions: just before the first positive scan, at the upper limit and in the steady state after a number of cyclic scans. It was found that the mass change on the electrode surface is the major factor contributing to the change in frequency, since the changes in the results obtained under the three conditions were negligible.

In summary, an increase in the mass of the Nafion[®] coating saturated with $[\text{Os}(\text{bpy})_3]^{2+}$ was observed during the first positive scan when excess $[\text{Os}(\text{bpy})_3]^{3+}$ complexes were ejected, and was ascribed to the ingress of water molecules. Osmosis into the Nafion[®] coating as a

result of the enhanced activity of water molecules inside the coating after oxidation of osmium complexes is considered to be a major factor contributing to this behavior. After a number of repeated potential cycles, the Nafion[®] coating reached a steady state in which the mass change during the potential scan was dominated by the transport of mobile counter-cations in the hydrated form.

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